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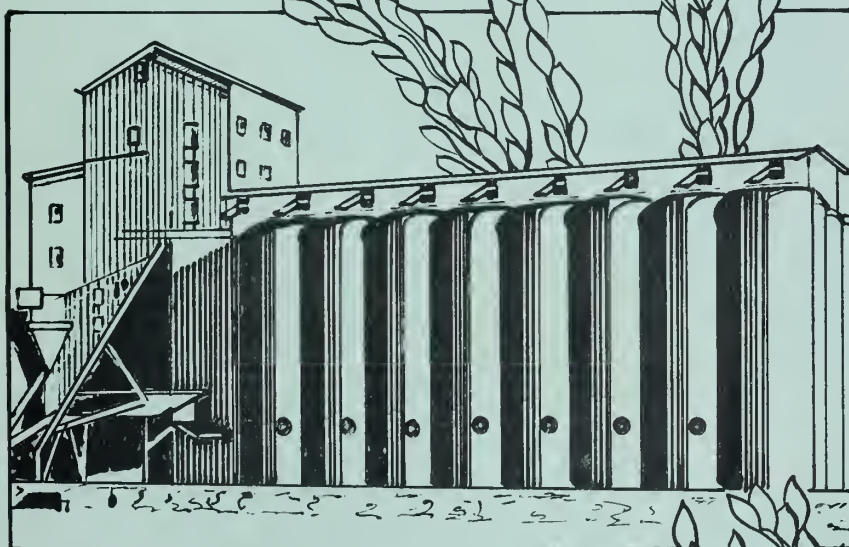
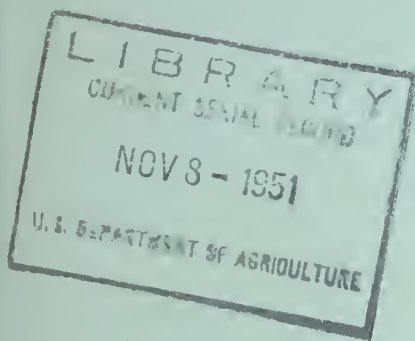
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THE CHEMICAL COMPOSITION OF RICE
A LITERATURE REVIEW

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Rice, Oryza Sativa L., is one of the world's oldest cultivated crops, predating 3,000 B.C., and the basic food of more people than any other cereal grain. The staple of over a third of the world's population, it is consumed principally in Asia where more than 90 percent of the total supply is produced. Rice was first produced commercially in this country in South Carolina in about 1685. By about 1887 the area in which rice was an important crop had shifted from the Atlantic seaboard to the Southern States. Today Louisiana is our leading rice-producing state followed by Texas, Arkansas, and California (34). In 1949 the United States produced 89 million bushels of rough rice. The domestic production could be materially increased if markets were available at satisfactory prices. However, economic studies (90, 245) indicate that the acreage should not be increased unless there is a considerable increase in the domestic consumption in view of the trend of the world market.

The production and marketing of rice have been described by Jenkins (34), Collier (32), and Yampolsky (242).

The three general types of rice grown in the United States are classified as short, medium, and long grain. Caloro, Colusa, Onsen, Pearl, and Cody which are grown mainly in California are typical of short grain varieties (32). Early Prolific, Zenith, Blue Rose, Magnolia, and Calady 40 are illustrative of medium grain varieties, and with the exception of the latter are grown in the Southern States. The long grain varieties, such as Rexoro, Nira, Texas Patna, Blue-bonnet, Fortune, Prelude, R.N., and Lady Wright, are grown almost entirely in the southern rice belt.

The rice grain is made up of the hull, the seed coat (pericarp), the embryo (germ), and the starchy endosperm. The seed coat consists of seven layers of differentiated types of cells, the last being the aleurone layer which is rich in proteins, oils, and vitamin B (233, 242). Borasio (23) showed by staining cross sections of the rice grain that no fats are present in the endosperm. Other investigators (see table IV) have found small amounts of lipids in polished rice.

Proteins and mineral salts are present in the aleurone cells and also in the outer starch containing cells.

^{1/} Report of a study made under the Research and Marketing Act of 1946.

^{2/} One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

By means of suitable milling equipment rice is separated into hulls, bran, and polished rice. Details of these operations are described by Kik (106). An evaluation of recent rice processing developments was made by Mickus (133). When only the hull is removed and the bran left intact, the product is referred to as brown rice. Rice from which the hull and bran have been removed is called polished rice, and it is in this form that rice is usually marketed. The polished rice is screened to remove broken particles. The unbroken kernels are referred to as head rice. The broken kernels are further separated by screening into second head, screenings, and brewer's rice, depending upon the degree of breakage. Rice bran and rice polish are important byproducts of the milling of rice. Commercial rice bran is composed primarily of the embryo and the outer three seed coat layers. Rice polish is composed of the inner seed coat layers along with some starchy material (105).

Table 1 shows the average yield of products and byproducts obtained from rough rice in the milling process.

Table 1. Average Yield of Products and Byproducts of Rough Rice
(As Received Basis)

Variety	Hulls	Bran	Polish	Head: Rice	Second: Head	Screen-: ings	Brewer's: Rice	Loss and Dirt
	%	%	%	%	%	%	%	%
Japan <u>1/</u>	17.4	8.4	3.0	56.9	3.0	5.4	3.0	2.9
Japan <u>2/</u>	18.5 <u>4/</u>	12.3	3.7	59.3		3.1	3.1	
Honduras <u>1/</u>	20.9	9.2	3.1	36.8	11.7	11.0	4.3	3.0
Honduras <u>2/</u>	20.4 <u>4/</u>	13.6	3.7	36.4	11.7	9.3	4.9	
Blue Rose <u>1/</u>	17.9	8.0	2.5	57.4	3.1	5.6	2.5	3.0
Unknown <u>3/</u>	20.0	8.5	1.8	57.8	2.6	6.0	2.1	1.2
Unknown <u>5/</u>	20.0	12.0	4.0	62.0				2.0
Unknown <u>6/</u>	19.0	8.0	3.0	65.0		3.0 <u>4/</u>	2.0	

- 1/ Calculated from data given by Fraps (56).
2/ Calculated from data given by Wise and Broomell (234).
3/ Kik (106).
4/ Includes "invisible" loss in hulling and milling.
5/ Davies (41).
6/ Morrison (141).

A study of rough rice of eight varieties grown in three locations showed variations in milling yields and in oil contents of bran and of the pericarp and germ fraction which are attributable to the influence of variety and environment of growth (92).

Tables 2,3, and 4 show the composition of rough rice, brown rice, and polished rice as reported by various workers. It is apparent that rice is high in carbohydrates and relatively low in protein.

Table 5 shows the composition of rice bran, rice polish, rice embryo, brewer's rice, and screenings. The values indicate that these products are valuable as feeding materials. Other constituents of rice include oil, ash, vitamins, and enzymes. The composition of rice will be discussed under the headings of the various constituents.

CARBOHYDRATES

For many years rice starch has been manufactured in Europe, principally in Belgium, Holland, and Germany. From about 1932 until about 1943 rice starch was produced commercially in the United States, but the manufacture of this product was discontinued because the cost made the operation unprofitable.

Rice starch granules are the smallest of commercial starches. The size of the granule is commonly 3-8 μ although the large granules may be from 8-10 μ (48, 100). The granules are angular and flattened and because of their small size, the characteristic features such as hilum, striations, and lines by polarized light are not distinct.

Because the rice starch granules are so small and are surrounded by an insoluble gluten, it is necessary to first soften the granules by chemical means. Orlando Jones (91) who operated a starch factory in London in 1840 patented a process which embodies the general principles of the processes now in use. The rice is steeped in a solution of caustic soda of 1.005 specific gravity, drained and steeped in water. More caustic is added and the steeping is continued. The rice is then ground with caustic soda solution and is allowed to settle or is centrifuged. The raw starch is washed in water, again allowed to settle, and then is drained and dried in blocks (51, 155, 230).

The small size of the granule makes rice starch desirable in laundering where good penetration and high finish are sought. The granules penetrate the fabric even in the ungelatinized state and when later they are gelatinized by ironing, they stiffen the fabric throughout. Rice starch is also used in confectionary and cosmetics, and for a variety of other purposes (224).

Mudaliar (142) investigated the presence of starch in the developing rice grain. He reported that starch is present in the ovary wall and the pericarp layers in the early stages of development but is exhausted as the grain develops. Starch has been found in the endosperm about 4 days after blooming and appears in the embryo about 7 days after blooming where it is present in abundance until about the twentieth day. After this time the starch in the embryo becomes exhausted, and by harvest time (about 30 days after blooming) only traces of starch have been found in the scutellum.

Table 2. Composition of Rough Rice

Source of data	Water :	Protein :	Fat :	N-Free :	Fiber :	Ash :	Starch :	Pentosans :
	%	%	%	%	%	%	%	%
Wiley (229)								
Minimum	9.0	8.2	1.4	65.0	9.4	3.3		
Maximum	11.5	8.4	2.0	65.7	11.5	4.7		
Joachim and Kendrich (85)								
Average	12.0	6.7	1.9	63.8	10.4	5.3		
Ross (164)	11.0	7.4	2.5	64.3	9.3	5.5		
Wise and Broomell (234)								
Honduras	11.3	7.5	1.6		8.7	5.4		5.9
Japan	11.1	6.5	1.7		7.9	5.1		5.5
Le Clere (122)	10.3	8.0	1.7	65.6	10.5	4.1		
Frops (56)								
Average of 9 Samples	11.7	8.1	1.8	64.5	8.9	5.0		
Morrison (141)	11.4	8.3	1.8	64.7	8.8			
Davies (41)	9.6	7.6	1.9	66.7	9.3	4.9		
Stubbs, Dodson and Browne (186)		9.9				69.7		2.1

Table 3. Composition of Brown Rice

Source of data	Water :	Protein :	Fat :	N-Free :	Fiber :	Ash :	Pentosans :
	%	%	%	%	%	%	%
Wiley (229)							
Minimum	10.9	7.3	1.6	73.3	0.9	1.0	
Maximum	12.6	10.5	2.3	77.3	1.3	1.2	
Joachim and Kamlich (85)							
Average	11.6	9.1	2.4	74.8	0.7	1.4	
Wise and Broomell (234)							
Honduras	12.3	8.6	1.8		1.0	1.2	2.4
Japan	12.4	7.2	1.5		0.9	1.1	2.3
Sridasivan and Sreenivasan (164a)							
	10.9	6.7	2.4	77.4	0.5	1.4	
Fraps (56)							
Average of 16 Samples	12.2	9.1	2.0	74.5	1.1	1.1	2.2
Morrison (141)							
	9.8	8.9	2.0	77.2	1.0		
Le Clerc (122)							
	9.3	7.9	2.2	78.6	0.8	1.1	

Table 4. Composition of Polished Rice

Source of data	Water	Protein	Fat	N-Free	Fiber	Ash	Starch	Pentosans
	%	%	%	%	%	%	%	%
Wiley (229)								
Minimum	11.8	5.4	0.04	75.6	0.3	0.3		
Maximum	13.2	10.3	0.5	81.7	0.6	0.7		
Joachim and Kendiah (85)	12.2	7.6	1.0	77.9	0.3	1.0		
Wise and Broomell (234)								
Honduras	12.1	8.2	0.2		0.3	0.3		1.8
Japan	12.7	6.3	0.2		0.3	0.4		1.7
Sadasivan and Sreenivasan (164a)	11.6	5.7	0.6	81.5	0.2	0.5		
Morrison (141)	12.2	7.4	0.4	79.1	0.4			
Davies (41)	12.3	7.4	0.4	79.0	0.4	0.5		
Stubbs, Dodson and Browne (186)		6.6					77.6	
Le Clerc (122)	9.4	7.4	0.3	82.3	0.1	0.3		

Table 5. Composition of Some Milling Products of Rice

Source of data	Water	Protein	Fat	N-Free	Extract	Fiber	Ash	Pentosans	Cellulose	Sugars	Sucrose
	%	%	%	%	%	%	%	%	%	%	%
Wise and Broomell (234)											
Hinluras	9.6	13.4	10.7			11.7	10.6	10.0			
Japan	9.4	12.8	15.1			12.5	11.3	11.4			
Joachim and Kandiah (85)	12.5	13.2	10.1	58.7		14.1	11.4				
Morrison (141)	8.9	12.8	13.4	41.1		13.0					
	10.3	11.6	16.2			9.6	14.3				
Marti (145)	11.1	10.6	10.6			10.1	20.6				
Davies (41)	10.1	12.1	11.4	44.3		12.4	9.7				
Fujita (57)	14.7	12.9	22.4				9.3	8.7	11.4	1.3	10.6
Maranon and Cosme (128)	11.7	12.5	19.8	39.3		6.3	10.4				
Morrison (141)	9.5	12.7	11.5	57.2							
Davies (41)	10.0	11.9	9.1	62.3							
Fraps (56)											
Average of 9 Samples	11.8	8.9	1.0	77.1		0.6	0.7				
Morrison (141)	12.0	7.4	0.6	78.4		0.8					
Borasio (27)											
Minimum	10.5	10.5	10.7	52.5		3.3	7.4				
Maximum	12.3	11.8	13.4	55.8		3.9	8.0				
Fraps (56)											
Average of 8 Samples	11.4	8.4	0.5	78.7		0.4	0.6				

Starch is the major component in the endosperm of rice. Analysis of 8 varieties grown at 3 locations gave an average of 89.8% starch in the polished rice on the moisture-free basis ^{2/}. Sreenivasan (183) gives the starch content of new rice as 82.0-85.7%, dextrose 1.66-3.06%, sucrose 0.34-0.55%, and dextrans 1.80-2.35% on the dry basis. No marked change is reported in the amount of carbohydrates during storage (183).

The ash content of native rice starch has been found to be from 0.13-0.30% (119, 193), including calcium, potassium, phosphoric acid, and silica. Tadokoro (193) reported that starch ash contains 9.3% phosphorous pentoxide and 18.1% silica.

Rice starch, in common with most other starches, contains both amylose and amylopectins. Tadokoro (193) determined amylose by an isolation method in which a 1% starch solution was frozen for 12 hours at a temperature of less than -10°C., after which the amylopectin appeared as a cloudy precipitate. The precipitate was filtered off, washed, dried, and weighed. The filtrate was concentrated and the amylose precipitated with alcohol, filtered, dried, and weighed. An average of 23.4% amylose was found for the starch of rice of 4 different varieties (193). More recent work using the iodine binding method (9) gives a much lower figure of 14-15%. It is felt that this figure is more accurate since the isolation procedure does not completely separate all of the amylopectin (30).

Rice starch has been reported to contain 17% amylohemiacellulose (67), and crude hemicellulose is present in the amount of about 1.2% (174). The hemicellulose of the endosperm of rice is apparently arabino-xylan. It is broken down by diastase to arabinose and xylan (63). Katayama (96) states that about 1% methyl pentosans occur in all rices and rice starches. König (119) also found 1.4% pentosans in rice starch. The pentosan of the rice starch probably is composed of araban (101).

Several investigators (30, 75) found the ratio of glucose residues per nonreducing end group for whole rice starch to be 23 to 24 by the periodate method and 25, 28, and 30 by methylation. Bell (10) reported that methylated whole rice starch contains 29 glucose radicals in the average unit chain.

^{2/} Unpublished data of the Analytical Section of the Southern Regional Research Laboratory.

The density of rice starch was found to be 1.646 as determined by an evacuation method (210). The viscosity of rice starch dispersions varies with rice variety, place of crop production, and with the time of boiling of their preparation. The viscosity is reported to increase with time of boiling the starch solution and after reaching a maximum to decrease with further boiling (193, 194). The temperature of gelatinization of rice starch has been reported to be from 74-80° C. (160), and that of glutinous rice starch about 60-65° C. (251).

Lehrman (123) reported that on hydrolysis of 5 pounds of rice starch 14.75 g. of mixed fatty acids was obtained of which 36% was palmitic, 35% oleic, and 29% linoleic. The average heat of combustion has been determined as 4100 small calories per gram of rice starch on the dry basis (193).

The pericarp of mature rice contains no starch (242). The syrup made from rice polishings contains 0.17% pentose (73). Sucrose, d-glucose, and d-fructose were also isolated from rice polishings (73). The total sugar in rice bran calculated as invert has been reported as 2.16-3.0% on the dry basis (145). An alcohol extract of the rice germ was found to contain 70% glucose, fructose, and sucrose and about 14% dextrin (180).

Polished rice has been found to contain 0.24-0.46% sugar and 0.85-1.06% dextrin (203). Only small quantities of cellulose have been reported in polished rice, the range being from 0.307-0.404% (208).

The variation of pentosan and uronic acid in rice during growth has been studied (113). Considering that a reciprocal relation holds between the quantity of pentosan and uronic acid, it is presumed that these two constituents are produced from hexose.

Maranon and Cosme (123) found 2.9% gum in rice bran.

NITROGENOUS CONSTITUENTS

Polished rice contains from 5.5-11.9% protein on the moisture-free basis (39, 56, 77, 229). This includes salt-soluble, alkali-soluble, and alcohol-soluble fractions. Jones and Gersdorff (89) failed to find any albumin in the polished rice. From the polished rice 4.16% glutelin (152), 0.07-0.09% globulin (89), and about 0.12% prolamine (76, 190) have been isolated. Rosenheim and Kajiura (94, 163) suggested the name oryzenin for the alkali-soluble glutelin which makes up the bulk of the protein present. Since pure rice protein contains an average of 16.8% nitrogen, a factor of 5.95 has been recommended (87) for converting the nitrogen of rice to protein. According to Tadokoro and Abe (196) the following changes in the nitrogenous constituents take place during the ripening of rice: the ratio of the amount of protein nitrogen to total nitrogen increases

while that of nonprotein nitrogen to total nitrogen decreases; the amounts of globulin and prolamine increase and the amount of water-soluble protein decreases; and oryzenin reaches its highest concentration shortly before ripeness at which time the maximum amount of glucose forming carbohydrates is present. These changes are the reverse of those which take place on germination.

Kondo and Hayashi (116) modified the technique of isolating proteins by using weaker solutions of sodium chloride to disperse the proteins. This caused less alteration of the protein during the process. They determined that the maximum flocculation point for rice glutelin occurs near the point of absolute neutrality. This point changes according to the concentration of salt in the solution. The sulfur content of glutelin is 0.55-0.89% and the phosphorus content is 0.11% as determined by Tadokoro (199). The sulfur content of alcohol-soluble protein was found to be 0.22%, of water-soluble protein 0.82%, and of sodium chloride-soluble protein 0.92% (197).

By dialysis of the saline extracts of polished rice a protein fraction has been isolated which contains two globulins coagulating at 74° and 90° C., respectively (89). Other workers (117, 118) also isolated two globulins from polished rice, one amorphous and one crystalline. The amorphous globulin was higher in diamino nitrogen, particularly in the form of histidine, cystine, and arginine than was the crystalline globulin. The pH of the isoelectric point of the globulin is 4.6-5.5 (80, 205).

Glutelin can be prepared from polished rice by precipitating a 0.2% sodium hydroxide extract with ammonium sulfate added to 0.3 saturation (88, 209). Unlike the globulin only one glutelin fraction has been obtained, the isoelectric point of this protein being at pH 6.45 (88). The specific rotation of rice glutelin at 20° C. in 0.5 M sodium hydroxide has been reported to be -65.1° (38).

The alcohol-soluble protein found in the polished rice contains less ammonia nitrogen and more basic nitrogen than is typical of prolamines. Only a small amount of the basic nitrogen is lysine nitrogen while the arginine content is higher than that of any other known prolamine (76, 190). The pH of the isoelectric point of this protein is 6.0-6.5 (205).

Kik (105) reported the proportion of nitrogen found by extracting polished rice successively with a series of solutions to include 91.04% of the total nitrogen. These values are shown in table 6. Similar results were obtained by Kondo (115) and Tadokoro (195, 198).

Table 6. Percentage of Total Nitrogen Extracted from Rice by Specified Successive Solvents (105)

Successive Extractions	Brown Rice	Polished Rice
1% sodium chloride solution	13.82%	11.51%
60% alcohol	3.66	5.75
0.1% alkali	44.22	40.85
Acidified alcohol	3.98	5.33
Hydrolyzed residue	25.90	27.60
Total	91.58%	91.04%

The nitrogen distributions in the proteins from polished rice are given in table 7.

Table 7. Nitrogen Distribution in Protein from Polished Rice (In Percent of Total Nitrogen)

Nitrogen	In Glutelin (88,116,152,206)	In Prolamine (76)	In Globulin Coagulating at 74°C. (89)	In Globulin Coagulating at 90°C. (89)
	%	%	%	%
Amide N	10.70 -- 11.33	12.45	6.91	7.79
Humic N	0.86 -- 1.59	1.65	1.41	0.73
Cystine N	0.88 -- 1.56	1.33	1.61	1.88
Arginine N	16.36 -- 21.80	13.21	15.48	27.23
Histidine N	3.68 -- 6.42	6.24	4.01	4.54
Lysine N	1.26 -- 7.35	1.73	8.39	3.88
Amino N of filtrate	52.13 -- 54.33	53.59	56.67	49.94
Non Amino N of filtrate	2.30 -- 5.28	7.32	5.50	3.81
Melanin N	2.02			

Van Veen (223) isolated several nitrogen-containing compounds from rice bran. These included guanine, xanthine, adenine, hypoxanthine, histidine, ammonia, dimethylamine, trimethylamine, cytosine, nicotinic acid, arginine, guanidine, betaine, choline, a mixture of mono amino acids and uracil (236). Allantoin is found in the extract of rice polish (222).

The distribution of non-protein nitrogen in brown rice as reported by Jodidi (85) is shown in table 8.

Table 8. Distribution of Non-protein Nitrogen in Brown Rice as Percentage of Total Nitrogen (86)

Variety	: Protein	: Non-protein	: Amino Acid	: Acid Amide	: Peptide
	: N	: N	: N	: N	: N
	%	%	%	%	%
Wateribume	95.33	5.02	0.75	0.14	0.85
Blue Rose	95.92	4.00	1.40	0.17	1.61
Honduras	97.12	4.02	1.02	0.23	1.15

The amino acid content of different varieties of rice (104, 105) varies considerably. Polished rice has been found to contain 0.073% cystine, 0.066% tryptophane, 0.280% lysine, 0.251% arginine and 0.059% histidine (105). Of these amino acids cystine is nutritionally essential only when methionine is present at too low a level, and arginine can be partly synthesized by the body. The others are nutritionally essential. Table 9 shows the amino acid content of rice protein and of various rice products and varieties. The amino acid content compares favorably with that of corn, wheat, and casein.

One fourth of the protein of whole rice is contained in the bran and polish. The aleurone layer and one or two layers of the cells of the endosperm adjacent to the aleurone layer are rich in protein (105, 156).

Rice bran contains 2.14-2.49% nitrogen (89, 105). Using the factor of 5.95 recommended by Jones (87) this would correspond to 12.5-14.8% protein.

According to Kik (105) rice bran contains 0.137% cystine, 0.096% tryptophane, 0.443% lysine, 0.344% arginine, and 0.090% histidine.

Rice bran contains salt-soluble, water-soluble, and alcohol-soluble protein. Though earlier workers (190) had reported the presence of glutelin in rice bran Jones and Gersdorff (89) were unable to confirm its presence. The globulin fraction consists of three globulins amounting to 2.88% of the bran (89) and coagulating at 75°, 84°, and 95°C., respectively. Analysis of this globulin preparation showed it to contain 2.23% cystine, 6.20% tyrosine, 3.28% tryptophane, 17.25% nitrogen, and 1.08% sulfur (89).

Table 9. Amino Acids in Rice and Rice Products (Calculated to 16.0% Nitrogen)

Source	Argi- nine	Histi- dine	Tyrosine	Tryptophan	Phenyl- alanine	Cystine	Methionine	Threonine	Iso- leucine	Valine
	%	%	%	%	%	%	%	%	%	%
Brown Rice (105)	3.3	0.8	3.4	1.0		1.3				
Polished Rice (105)	3.9	0.9	4.4	1.0		1.0				
Bran (105)	2.6	0.7	3.3	0.7		1.0				
Polish (105)	2.2	0.6	3.0	0.9		1.1				
Rough Rice of different varieties (105)										
Arkansas 155	3.4	0.6	3.6	0.7						
Acadia	4.2	0.6	4.1	1.1						
Shoened	3.7	1.1	4.2	1.1						
Zenith	3.9	0.9	3.9	0.9						
Fortuna	3.5	0.9	5.1	1.1						
Rice Protein (22)	7.2	1.5	3.2	1.3	6.3	1.3	3.4	3.9	7.7	5.1
Oryzenin 1/ (152)	8.8	3.2	4.1	5.6						6.4

1/ Purified glutelin from polished rice.

Two albumins coagulating at 65° and 70° C. and amounting to 0.13% of the meal were isolated (89). Analysis of this combined fraction of albumin gave 16.28% nitrogen, 1.19% sulfur, 3.58% cystine, 5.08% tyrosine, 3.28% tryptophane, and 0.19% threonine (89, 121). An alcohol-soluble fraction was obtained from the bran which contained 11.2% nitrogen and 11.59% ash (89).

Guanine, adenine, xanthine, and hypoxanthine have been isolated in a pure state from rice embryo (72). Kimura (111, 112) prepared nucleic acid from rice embryo.

VITAMINS

Most of the vitamins present in rice are located in the bran which is removed in the process of milling. In the milling of brown to polished rice 40-80% of the thiamine, 50-56% of the riboflavin, and 63% of the niacin are lost (102, 103, 140). The thiamine and riboflavin content differs among varieties and to a slight extent with location of growth. The niacin content varies slightly with variety, but the variation is insignificant with location of growth (103). Table 10 shows the average values reported for the vitamins in rice products.

Vitamin B complex is present in both the bran (which includes the embryo) and endosperm of the rice kernel. The embryo end seems richer in this vitamin than the endosperm end of the kernel (35). It has been determined (166) that 66% of the B₁ is in the germ, 29% in the pericarp, and 5% in the endosperm of the rice. The range present is from trace quantities to 301 gamma/100 g. (31, 43, 163). Polished rice has been found to contain a significant amount of vitamin B₆ (167). Rice polishings are rich in vitamin B complex with the exception of vitamin B₂ (144). Nicotinic acid has been reported to increase by 17% in 9 days of germination (97).

The B₁ content of glutinous rice has been found to be quite high, the black varieties being higher than the white (500-600 international units/500 g.) (181).

Free and combined pyridoxine is present in rice bran extract (175) and Snell (179) claims that most of the vitamin B₆ activity of rice bran concentrate is due to pyridoxine. Greene (61) isolated crystalline vitamin B₆ from rice bran extract. Only small amounts of pyridoxamine and pyridoxal are present (179). Very small amounts of an unknown growth factor required by chicks has been found in rice polishings (185). Another unidentified factor necessary in the prevention of acrodynia has been found in this material (188). This may be vitamin B₆. A chloroform-water extract of rice polishings contains a factor which inactivates thiamine in vitro (19). This factor is nonenzymic in nature, and on dialysis is separated into a heat labile and a heat stable fraction both of which are active against thiamine.

Table 10. Vitamins Present in Rice

Vitamin	:Rough : :Rice :		:Brown : :Rice :		:Polished : :Rice :		:Bran : :		:Polish:Embryo:Glutinous:Parboiled: : : : Rice : Rice :		Reference		
µg per gram on moisture-free basis													
Thiamine	3.35		2.00-4.80		trace-3.01		27.9		23.3	54.20	3.19	0.78	(31,43,98, 102,157, 168,172,232,250)
Nicotinic Acid			46.2-47.2		12.7		408.6		384.7				(232)
Pantothenic Acid			10.3-17.0		6.4		71.3		92.5				(232)
Pyridoxine			10.3		4.5		32.1		30.8				(232)
Riboflavin	0.73		0.60-0.61		0.24-0.26		2.14-4.00		1.8				(7,102)
Biotin			0.121		0.042		0.468		0.66				(231)
Niacin	53.40		53.08		19.62								(103)
Vitamin E			29				30			Present			(50,70,107)
Vitamin C			18										(21)

Maiocco (126), Kimm (107), and Todd and co-workers (214a) reported the presence of vitamin E in rice.

Rice may be parboiled or converted to improve its nutritive value. Parboiling involves the treatment of the unhulled rice with hot water and steam. Conversion is a similar process in which steam is applied under pressure to unhulled rice which has previously been held under a slight vacuum (148, 248). Kik (102) found that conversion favors the retention of thiamine, riboflavin, and niacin. Thiamine seems quite stable on storage. Hinton (71) showed that there is an appreciable movement of vitamin B₁ from the embryo into the endosperm as a result of parboiling. Parboiled rice is generally poorer in fat than raw rice polished to the same degree (184). According to Sreenivasan (182) there is a considerable movement of the fat constituents from the germ into the bran. On parboiling, part of the nitrogen and phosphorus present in the germ is transferred to the endosperm (187). Parboiling partially gelatinizes the endosperm and the germ is not as readily removed in the milling process (148). Mickus (133) found parboiled rice more desirable for canning purposes.

Methods of preparation of vitamin B₁ from rice have been given by Greene and Black (62) and Cook and Carroll (34).

Aykroyd (6) found a correlation between the phosphorus content and vitamin content of rice. However, another investigation (139) showed the vitamin B₁ content of rice to be independent of its phosphorus content. The same investigation showed the vitamin content of the rice seems to decrease with the age of the rice.

Although Tanaka (212) and Miki (134) found that rice embryo contains vitamin A, according to de Sacy (47) there was not enough of this vitamin in whole rice to support rats or pigeons.

RICE BRAN OIL

Rice bran oil is found in the bran and in the polish to the extent of about 8-17% (83, 129, 227). The oil of rice bran has a dark green chlorophyll color (227, 247).

A lipolytic enzyme present in the bran becomes active when the bran is separated from the rice, thus causing the free fatty acid content of the oil in the bran to increase rapidly (29). The free fatty acid content, ordinarily below 3% immediately after milling, increases at the rate of about 1% an hour (159) during the first few hours. This is a disadvantage in the production of a commercial edible oil and necessitates the immediate treatment of the bran -- either by extraction, drying, steaming or chemical treatment -- to prevent this free fatty acid formation (159, 249). It has been found that decreasing storage temperature of bran tends to retard free fatty acid formation (124). Also, if the bran is sufficiently dried and maintained at a low moisture content, the increase of free fatty acid content is retarded (124).

By extracting fresh rice bran with commercial hexane a crude oil of low free fatty acid content can be obtained (159, 192). This oil can be refined and bleached by standard methods to give a high-grade edible oil. Its smoke, flash, and fire points compare favorably with other edible oils; it is resistant to oxidative rancidity; it can be easily winterized; and the keeping quality of the hydrogenated product is superior to that of cottonseed and peanut oils (52).

The physical and chemical characteristics of rice bran oil are given in table 11.

Table 11. Physical and Chemical Characteristics of Rice Bran Oil

Characteristic	Value	Reference
Specific gravity at 15/15° C.	0.918-0.928	(1, 138)
Specific gravity at 25/25° C.	0.912-0.920	(1, 138)
Refractive index at 40° C.	1.465-1.468	(1, 138)
Iodine value	92-109	(1, 138)
Thiocyanogen value	68-70	(42)
Saponification value	179-194	(42)
Unsaponifiable matter (%)	3.0-5.0	(1, 138)
Titer, °C.	27-29	(159)
Acetyl value	8.0-10.0	(1, 138)
Reichert-Meissl value	0.3-1.7	(83)
Polenske value	Below 0.5	(1, 138)
Saturated acids, %	15-18	(1, 138)
Unsaturated acids, %	76-82	(1, 138)
Smoke point	415°F.	(52)
Flash point	615°F.	(52)
Color (crude oil)	Yellow 35, red 6.0	(215)
Solidifying point	+2 to -10	(42)

The liquid fraction of the rice bran oil is 61-74.3% and the solid fraction 27-39% of the total oil (44, 83, 227). The liquid portion contains about 91% fatty acids and the solid portion about 90.6% fatty acids (227).

Rice bran oil consists principally of the glycerides of the unsaturated fatty acids oleic (219) and linoleic (220) and the saturated acid palmitic (36, 219). Also present in smaller amounts are arachidic, myristic, stearic, lignoceric, and behenic (207). An unsaturated acid $C_{24}H_{48}O_2$ or $C_{26}H_{52}O_2$ is also present (220).

The composition of rice bran oil is shown in table 12.

Table 12. Composition of Rice Bran Oil

Fatty Acid	Literature Reference							
	(37)	1/(36)	1/(83)	1/(216)	2/(207)	2/(220)	2/(42)	2/
	%	%	%	%	%	%	%	%
Myristic	0.2	0.1	0.3					
Palmitic	17.3	16.9	12.3	20.0				
Stearic	1.8	2.6	1.8					
Arachidic	0.7	0.5	0.5					
Behenic					0.5-0.6			
Lignoceric	0.7	0.9	0.4					
Oleic	45.6	45.3	41.0	45.0	42.6-47.2	52.8		39-44
Linoleic	27.7	27.6	36.7			35		27-35
Unsaponifiable matter	4.0	4.0	4.6					

1/ Percent glycerides in original oil.

2/ Calculated as fatty acids in fatty acids isolated from rice bran oil.

In rice milling Nisiyama (149) found that the oil from the inner layers of the rice bran showed more fluidity, increased saponification value, lower acid value, higher ester value, and higher iodine value than the oil from the outer layers.

The unsaponifiable matter makes up about 3.0-5.7% of rice oil (5, 36, 44, 83, 146, 215). Sterols are present in the unsaponifiable matter to the extent of about 25% (83). About 5.3% unsaponifiable matter is found in the liquid portion of the oil and 4.7% unsaponifiables in the solid portion (227). Crystals of phytosterol have been isolated from the unsaponifiable fraction of rice oil (216) in the amount of 2.7% of the original oil (5). Other sterols present in the unsaponifiable matter include dihydrositosterol and stigmasterol (2, 3, 83, 146). From 6-9% of the sterols in rice oil are unsaturated (173).

Small amounts of a saturated hydrocarbon, m.p. 79.5-80.5° C., for which the empirical formula $C_{27}H_{48}$ is suggested, can be separated from the unsaponifiable fraction⁴⁸ of the oil (227). Also present in this fraction are small quantities of myricyl alcohol (146) and ceryl alcohol (218). Fitelson reports the presence of 332 mg. of squalene per 100 g. of fat from rice bran (54).

The total lipids from rice contain 3-9% of wax, which is reported to be largely melissyl cerotate. The wax is not extracted by hexane at temperatures below 10°C. (159, 213).

Rice oil contains exceptionally potent antioxidants which render it resistant to oxidation before and after hydrogenation. The presence of the following antioxidants in rice bran oil has been reported: 0.026% γ - and 0.075% α -tocopherol in the crude oil and 0.033% γ - and 0.058% α -tocopherol in the refined oil (53). A potent antioxidant which is dialyzable and partly soluble in linoleic acid has been found in an aqueous extract of rice bran. This antioxidant is not fat-soluble or ether-soluble (65, 66).

The rice embryo contains an average of 24% fatty matter. Of the fatty acids present 25% are saturated and 75% unsaturated. The saturated acids include palmitic, arachidic, behenic, myristic, and stearic. The unsaturated acids consist almost exclusively of oleic and linoleic (74, 108, 109, 110).

Kimm (108) found 5.28% unsaponifiable matter in the oil from rice embryo. This fraction contains melissyl alcohol, ergosterol, dihydrositosterol, stigmasteryl, γ -sitosterol, a sterol melting at 156°C., β -tritosterol, α - and β -tocopherol, β -amyrin, a hydrocarbon $C_{15}H_{16}$ and a phytosterolin (107, 108, 109, 111).

The wax of rice embryo is composed mainly of melissyl cerotate (108). A cerebroside-like substance was also obtained from the benzene extract of the embryo (108).

On extraction of rice embryo with hot 90% alcohol and saponification of the extract, the benzene soluble portion was found to give a positive estrone test (8).

Sebe (176) reported that 0.5% of the total oil from rice embryo is volatile and is a mixture of 90% hydrocarbons and a small amount of lower fatty acids and alcohols. The paraffin hydrocarbons consist of homologs of C_{10} — C_{16} and the aromatic hydrocarbons consist of monoalkyl benzenes, α -dialkyl benzenes, naphthalene, p-methylnaphthalene and dimethylnaphthalene (176). Nakamiya (147) obtained from the unsaponifiable fraction of rice embryo oil an unsaturated hydrocarbon whose formula is $C_{18}H_{32}$.

Inasmuch as the embryo makes up a portion of the bran, it can be assumed that the components of the embryo are also found in the bran.

ENZYMES

Very little modern research on the enzymes of rice has been conducted. The older research in this field is reviewed, even though it is realized that some of it is out of date, for purposes of providing a background for anyone who cares to go into the older literature on the enzymes of rice.

Amylosynthase is present in the rice mainly in the endosperm (135, 136, 137). This was proved by preparing from polished rice a strongly amylosynthetic but weakly amolytic enzyme solution. Giri and Sreenivasan (59) report that there is apparently no active amylase in polished rice. They hypothesized that in ungerminated rice kernels the amylase is largely in an adsorbed condition which inactivates it. When rice kernels are extracted with phosphate buffers in the range of pH 6.8-8.0, the extracts so obtained exhibit saccharifying and dextrinizing activity. Two amylases are present, an α -amylase with optimum activity at pH 7 and a β -amylase with optimum activity at pH 4.6 (59). A starch-liquefying enzyme is also present (60, 241) which is more thermostable than the dextrinizing and saccharifying amylase (241). During the ripening process both enzymes become gradually inactive, and in completely ripe rice can no longer be extracted with water. During germination the activity of these two enzymes increases (165) and the difference between the water and phosphate extractable fractions becomes less. The pure α - and β -amylases are transformed during germination into the amylase system ($\alpha+\beta$) which is characteristic of malt (59). The optimum temperature for the activity of the amylase has been reported to be 60° C. (95).

In unpolished rice also, evidence was found of the presence of an amolytic enzyme (135, 136, 137). Amylase has been obtained from rice polishings and embryo, but Minagawa (137) reported no evidence of the presence of amylosynthase in this part of the rice.

Freshly harvested rice has not been found to digest as readily as stored rice. Fresh rice is thought to have an active α -amylase which causes it to have a sticky consistency after cooking (244).

The endosperm of the rice grain is rich in zymogen which can be extracted with salt solution (237, 238).

Fractions exhibiting ascorbic acid oxidase action (201), dehydrogenase action (200, 201, 203), and peroxidase action (202) have been isolated from the rice germ. On storage the oxidase activity of rough rice remains constant but the amylase, lipase, catalase, and peroxidase activity decreases (150). Pyrogallol oxidase is absent from unmalted rice but develops during germination (225). Rice, like corn, wheat, and barley, also contains an inhibitor which interferes with the oxidation of pyrogallol (225).

There is an indication of a relationship between germinative capacity and the catalase content of the seed in that the presence of catalase decreases with the age of the seed (170, 246). Borasio (23), however, was unable to confirm any such a relationship.

Water-soluble phosphomonoesterases have been prepared from rice bran (221). There are three such enzymes exhibiting activity at pH 3, pH 5.5, and pH 9 (151). The presence of a phosphodiesterase has also been reported (221).

The starch-liquefying action of the aqueous extract of the seed coat of the rice is more active than that of the endosperm (240). The optimum pH for the activity of the starch liquefying enzyme in the water extract of unhulled rice was 5.2-5.4 and for unpolished rice, rice bran, and embryo 4.8 (239).

Rosedale and Oliveiro noted the presence in the extract of rice bran of invertase and a lipolytic enzyme (162). The lipase is a troublesome factor, for unless it is inactivated, it causes the free fatty acid content of the oil to increase considerably thus necessitating prompt extraction of the oil.

Phosphatase and phytase have also been found in the bran (33, 49).

Analytical values for protease activity in the whole rice equivalent to 0.7% trypsin have been reported (58).

As early as 1835 the presence of diastase (amylase) was recognized in the germinating grain (153). Other enzymes in germinated rice include α -glucosidase, β glucosidase, sucrase, pectinase, glycerophosphatase, lecithinase, and esterase (143). The enzymes are shown to be localized mostly in the seed coat of the rice (24).

PHOSPHORUS COMPOUNDS

Only 0.14% phosphorus has been found in the polished rice (214). Most of it is found in the embryo and bran. A study of nitrogen and phosphorus distribution in the embryo and pericarp fractions of the brown rice showed that more than 50% of the phosphorus and 20% of the nitrogen are localized in these two fractions (187). Thompson (214) reported the absence of phytin in polished rice, but Borasio (26) found 0.13% present. The phosphorus content of the bran fraction ranges from 1.86 to 2.91% (130, 214). Only a small fraction of this is inorganic phosphorus (19% for the rice bran and 10% for the rice polish) (158). Most of the remaining phosphorus exists as phytin (130, 158, 189, 191, 214). Lüers and Silbereisen (125) isolated 4.2 grams of phytin from 1 kilogram of rice bran. They found this phytin to contain 1.6% inorganic phosphorus and 26.8% total phosphorus calculated as the pentoxide. Rather (158) reported that the phytin phosphorus occurs as salts of inositol pentaphosphoric acid. Phytin extracted by 0.3% hydrochloric acid was partly destroyed by the phytases of the grain. In order to obtain complete extraction 3% hydrochloric acid must be used (49). The organic phosphorus salts extracted from rice polishings were found to contain 19.5% phosphorus, 2.20% calcium and 11.22% magnesium (130). In addition, small amounts of lecithinic, lecithidic and nucleinic phosphorus have been reported (11).

MINERALS AND ASH

The inorganic constituents of rice are shown in table 13. The ash value of polished rice is about 0.5% (243) and that of brown rice varies from about 1% to 1.8% (99, 127, 131). Environment has little effect on the mineral content of the grain (127). According to Itano et al. (79) more than 65% of the iodine in the whole rice is found in the bran fraction of the grain.

The ash of brown rice is high in potash and phosphoric acid (99).

RICE HULLS AND STRAW

Rice hulls, because of their high silica content, are not suitable for feedstuff, but when finely ground the rice hulls serve as a good polishing powder.

Purified cellulose has been prepared from rice hulls which has an ash content of about 1% and a high percentage of α and hydrated cellulose (68, 69). On hydrolysis of rice hulls 16.2% reducing sugars were obtained (46). Samec (169) obtained 48% reducing sugars by hydrolysis with 10% sulfuric acid.

Some products of destructive distillation of rice hulls were investigated by de Leon and Reyes (45). They obtained charcoal, pyroligneous acid, tar, methyl alcohol, acetic acid, formic acid, phenol, and gaseous products.

By hydrolysis with 5% sulfuric acid, 4.19% furfural was obtained from rice hulls (46).

Iwata (81) investigated the composition of rice straw and found the content of digestible organic matter to be 40.9%, lignin 14.7%, and starch 20.7%. The cellulose content of rice straw varies from 32-59% (13, 161, 177).

Bertrand and Brooks (13) found rice straw to contain 26.60% xylose and 58.80% cellulose. The following analytical data were obtained on cellulose isolated from rice straw: yield 32%, water 8.4%, ash 1.0%, total nitrogen 0.07%, furfural 13.4%, copper value 1.1, cellulose number 0.56, α cellulose 76.4% and β cellulose 21.9% (114). Analytical values for hulls, straw, and hull ash are shown in tables 14 and 15.

Table 13. Mineral Constituents of Rice and Rice Products (moisture-free Basis)

Constituent:	Rough : : Rice :	Brown : : Rice :	Polished : : Rice :	Bran : : Rice :	Polish : : Rice :	Rice : : Rice :	Brewer's : : Rice :	Hulls : : Rice :	Straw : : Rice :	Ash : : Rice :	Miscel : : Rice :	Reference
	%	%	%	%	%	%	%	%	%	%	%	
Aluminum		0.03			0.00014							(14, 131)
Arsenic		0.008										(82)
Calcium	0.072	0.0096-			0.0042-		0.044	0.045	0.087	0.20		(4, 55, 85, 131, 141)
		0.0178			0.011							(4, 55)
Chlorine		T-0.002			T-0.027							(15, 16)
Cobalt					0.0000006		0.0008					(55, 64, 132, 154, 171)
Copper		0.00023-			T-							(178)
		0.00064			0.00019							(4, 55, 131, 132, 243)
Iodine					0.0000092							(4, 55, 131)
Iron		0.0031-			0.00043-		0.0171					
		0.034			0.0013							
Magnesium		0.047-			0.0131							
		0.12										
Manganese		T-			0.00096-		0.0112				0.0165	(4, 40, 78, 131, 132, 154)
		0.0015			0.001							
Nickel					0.0000017							(15, 16)
Phosphorus	0.236-	0.104-			0.102-		1.20	0.11	0.087-	0.075		(55, 131, 141)
	0.308	0.351			0.112				0.246			
Potassium	0.25	0.238			0.046-		1.30		0.34	1.36-		(4, 55, 85, 131, 141, 226)
					0.128					1.94		
Silica		0.032-										(4)
		0.112										
Sodium		0.020			0.0072							(55, 131)
Sulfur					0.0891							(55)
Titanium					T		0.0026				0.0149	(17, 18)
Zinc					0.00029-		0.00333					(12, 132)
					0.00075		0.0076					

Table 14. Composition of Rice Hulls and Rice Straw

Source of data	Water	Protein	Fat	N-Free	Fiber	Ash	Pentosans
	%	%	%	%	%	%	%
<u>Hulls</u>							
Fraps (56)	8.5	3.6	0.9	29.4	39.1	18.6	
West and Cruz (228)							
Ramai	7.7	1.8	0.6	32.7	35.0	22.3	
Macan	6.8	2.0	0.6	30.0	38.9	21.7	
Morrison (141)	8.0	3.0	0.8	28.4	40.7		
Davies (41)	9.3	3.3	1.1	34.0	35.4	16.9	
Stubbs, Dodson and Browne (186)	9.0	3.5	0.5	27.9	41.9	18.3	17.2
<u>Straw</u>							
Morrison (141)	7.5	3.9	1.4	39.2	33.5		
Stubbs, Dodson and Browne (186)	10.8	3.3	0.6	38.3	32.9	14.0	15.8

Table 15. Analysis of Rice Hull Ash (moisture-free Basis)

Source of data	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	P ₂ O ₅	SO ₃	SiO ₂	Cl
	%	%	%	%	%	%	%	%	%
Wolff (235)	1.60	1.58	1.01	1.96	0.54	1.86	0.92	89.71	
König (120)	1.53	0.30	0.51	0.07	0.45	2.69	0.42	93.21	0.15
Fraps (56)			0.86	0.28		0.36		95.49	
West and Cruz (228)			0.57	0.12		0.57		96.97	
Borasio (25)			0.25	0.23		0.53		94.50	

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